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**Membrane process for separation of organic liquids.**

A charge composition containing (i) an alcohol having less than three carbon atoms and (ii) an oxygenate selected from organic ethers, aldehydes, ketones, and esters is passed into contact with a first side of a non-porous membrane separating layer comprising a blend of a polyvinyl alcohol and a polyacrylic acid on a polyacrylonitrile support layer; with a pressure drop across the non-porous separating layer from the first (high pressure) side to a second (low pressure) side. At least a portion of alcohol from the charge composition and a lesser portion of oxygenate pass by pervaporation through the non-porous separating layer as a lean mixture containing more alcohol and less oxygenate than are present in said charge composition, leaving a rich liquid containing less alcohol and more oxygenate than are present in said charge composition; the lean mixture, in vapor phase at a pressure its vapor pressure being recovered as permeate from the low pressure side of the non-porous separating layer.

## MEMBRANE PROCESS FOR SEPARATION OF ORGANIC LIQUIDS

As is well known to those skilled in the art, it is possible to separate mixtures of liquids by various techniques including adsorption or distillation. These conventional processes, particularly distillation, are however characterized by high capital cost. In the case of distillation for example, the process requires expensive distillation towers, heaters, heat exchangers (reboilers, condensers, etc.), together with a substantial amount of auxiliary equipment typified by pumps, collection vessels, vacuum generating equipment, etc.

Such operations are characterized by high operating costs principally costs of heating and cooling -plus pumping. etc.

Furthermore the properties of the material being separated, as is evidenced by the distillation curves, may be such that a large number of plates may be required, etc. When the charge components form an azeotrope, additional problems may be present which for example, could require that separation be effected in a series of steps (e.g. as in two towers) or by addition of extraneous materials to the system.

There are also comparable problems which are encountered in adsorption systems.

It has been found to be possible to utilize membrane systems to separate mixtures of liquids by pervaporation. In this process, the charge liquid is brought into contact with a membrane film; and one component of the charge liquid preferentially permeates the membrane. The permeate is then removed as a vapor from the downstream side of the film - typically by sweeping with a carrier gas or by reducing the pressure below the vapor pressure of the permeating species.

Illustrative membranes which have been employed in prior art techniques include those set forth in the following table:

TABLESeparating LayerReferences

- Polyvinyl alcohol  
containing glycerine

- Kuraray Co. Japanese  
Patent 81/193495 (1981)  
JP 58/g5522A2 (1983)

- Nafion brand of  
perfluorosulfonic acid

- Cabasso and Liu  
J. Memb. Sci. 24, 101  
(1985)

- Sulfonated polyethylene

- Cabasso, Korngold  
& Liu, J. Pol. Sci.:  
Letters, 23, 57 (1985)

- Fluorinated Polyether  
or Carboxylic Acid  
Fluorides

- USP 4,526,948  
to DuPont as assignee  
of Resnick

- Selemion AMV  
blend of Asahi Glass  
cross-linked styrene  
butadiene (with quaternary  
ammonium residues on a  
polyvinyl chloride backing

- Wentzlaff  
Boddeker & Hattanbach  
J. Memb. Sci. 22,333  
(1985)

- Cellulose triacetate

- Wentzlaff, Boddeker  
& Hattanback,  
J. Memb.  
Sci. 22, 333 (1985)

- Polyacrylonitrile or  
Polytetrafluoroethylene  
grafted with N-vinyl  
pyrrolidone

- Neel, Aptel &  
Clement Desalination  
53, 297 (1985)

5 - Cellulose Acetate  
and others

- Proc. of Int. Mem.  
Conf. Sept., 1986  
Ottawa, p 229

10 - Crosslinked  
Polyvinyl Alcohol

- Eur. Patent 0 096  
339 to GFT as  
assignee of Bruschke

15 - Poly(maleimide-  
acrylonitrile)

- Yoshikawa et al  
J. Pol. Sci. 22, 2159  
(1984)

20 - Dextrine -  
isophoronediiisocyanate

- Chem. Econ. Eng.  
Rev., 17, 34 (1985)

25 The cost effectiveness of a membrane is determined by the selectivity and productivity. Of the membranes commercially available, an illustrative membrane of high performance is that disclosed in European patent 0 096 339 A2 of GFT as assignee of Bruschke - published 21 December 1983.

30 European Patent 0 096 339 A2 to GFT as assignee of Bruschke discloses, as cross-linking agents, diacids (typified by maleic acid or fumaric acid); dihalogen compounds (typified by dichloroacetone or 1,3-dichloroisopropanol); aldehydes, including dialdehydes, typified by formaldehyde. These membranes are said to be particularly effective for dehydration of aqueous solutions of ethanol or isopropanol.

35 This reference discloses separation of water from alcohols, ethers, ketones, aldehydes, or acids by use of composite membranes. Specifically the composite includes (i) a backing typically about 120 microns in thickness, on which is positioned (ii) a microporous support layer of a polysulfone or a polyacrylonitrile of about 50 microns thickness, on which is positioned (iii) a separating layer of crosslinked polyvinyl alcohol about 2 microns in thickness.

40 Polyvinyl alcohol may be cross-linked by use of difunctional agents which react with the hydroxyl group of the polyvinyl alcohol. Typical cross-linking agent may include dialdehydes (which yield acetal linkages), diacids or diacid halides (which yield ester linkages), dihalogen compounds or epichlorhydrin (which yield ether linkages) olefinic aldehydes (which yield ether/acetal linkages), boric acid (which yields boric ester linkages), sulfonamidoaldehydes, etc.

See also J. G. Prichard, Polyvinyl Alcohol, Basic Properties and Uses, Gordon and Breach Science Publishers, New York (1970) or

45 C. A. Finch, Polyvinyl Alcohol, Properties and Applications, John Wiley and Sons, New York (1973).

It is an object of this invention to provide a separation process. Other objects will be apparent to those skilled in the art.

In accordance with certain of its aspects, this invention is directed to a method of treating a charge composition containing (i) an alcohol having less than three carbon atoms and (ii) an oxygenate selected from the group consisting of organic ethers, aldehydes, ketones, and esters which comprises  
50 maintaining a non-porous membrane separating layer of a blend of a polyvinyl alcohol and a polyacrylic acid on a polyacrylonitrile support layer;

maintaining a pressure drop across said non-porous separating layer;

60 passing a charge composition containing (i) an alcohol having less than three carbon atoms and (ii) an oxygenate selected from the group consisting of organic ethers, aldehydes, ketones, and esters into contact with the high pressure side of said non-porous separating layer whereby at least a portion of said alcohol in said charge composition and a lesser portion of oxygenate pass by pervaporation through said non-porous separating layer as a lean mixture containing more alcohol and less oxygenate than are present in said

charge composition and said charge composition is converted to a rich liquid containing less alcohol and more oxygenate than are present in said charge composition;  
 recovering as permeate from the low pressure side of said non-porous separating layer said lean mixture containing more alcohol and less oxygenate than are present in said charge composition, said lean mixture  
 5 being recovered in vapor phase at a pressure below the vapor pressure thereof; and  
 recovering as retentate from the high pressure side of said non-porous separating layer said rich liquid containing a lower alcohol content and a higher oxygenate content than are present in said charge composition.

The composite structure which may be used in practice of this invention includes a multi-layer  
 10 assembly which in the preferred embodiment preferably may include a porous carrier layer which provides mechanical strength and support to the assembly.

#### THE CARRIER LAYER

This carrier layer, when used, is characterized by its high degree of porosity and mechanical strength. It may be fibrous or non-fibrous, woven or non-woven. In the preferred embodiment, the carrier layer may be a porous, flexible, woven fibrous polyester.

20 One typical woven polyester carrier layer may be formulated of woven, bonded strands.

#### THE POROUS SUPPORT LAYER

The porous support layer which may be used in practice of this invention is preferably formed of a sheet or membrane of polyacrylonitrile polymer. Typically the polyacrylonitrile may be of thickness of 40-80 microns, say 50 microns and of molecular weight  $\bar{M}_n$  of 5,000-100,000, preferably 20,000-60,000, more preferably 20,000-70,000 say 40,000. The polyacrylonitrile is preferably characterized by a pore size of less  
 30 than about 500Å and typically about 200Å. This corresponds to a molecular weight cut-off of less than about 50,000, typically about 40,000.

#### THE SEPARATING LAYER

The separating layer which permits attainment of the separation in accordance with this invention includes a non-porous film of a blend of a polyvinyl alcohol and a polyacrylic acid.

In accordance with certain of its aspects, when the separating layer is a blend or a mixture of vinyl  
 40 alcohol polymer and a polymer of an acrylic acid such as acrylic acids of methacrylic acid, the charge from which the separating membrane is to be prepared may be an aqueous solution containing a vinyl alcohol polymer and a polymer of an acrylic acid. Typically the aqueous solution may contain 5-10 w%, say 7 w% of polyvinyl alcohol of molecular weight  $\bar{M}_n$  of 20,000, more preferably 96,000-115,000 say 115,000 and 5-10 w%, say 7 w% of polyacrylic acid of molecular weight  $\bar{M}_n$  of 90,000 - 300,000, more preferably 90,000-  
 45 250,000 say 250,000. The weight ratio of vinyl alcohol polymer to acrylic acid polymer may be 0.1 - 10:1, say 1:1.

The composite membrane, prepared from the blend of a polyvinyl alcohol and a polyacrylic acid, may be cured in an oven at 100°C - 175°C, say 125°C for 1-30 minutes, say 8 minutes to yield a film having a thickness of 1-10 microns, say 2 microns.

50 It is possible that during curing, the polyvinyl alcohol and the polyacrylic acid may crosslink or otherwise react to form ester linkages.

#### THE PERVAPORATION MEMBRANE

It is a feature of this invention that the composite membrane used in the process of this invention may typically comprise (i) an optional carrier layer, characterized by porosity and mechanical strength, for

supporting a porous support layer and a separating layer, (ii) a preferred polyacrylonitrile porous support layer of molecular weight of 5,000 - 100,000, of thickness of 10 - 80 microns, and of molecular weight  $\bar{M}_n$  cut off of 25,000 - 50,000, and (iii) as a non-porous separating layer a blend of a polyvinyl alcohol and a polyacrylic acid.

5 The membranes of this invention may be utilized in various configurations. It is, for example, possible to utilize the composite in a plate-and-frame configuration in which separating layers may be mounted on the porous support layer with the carrier layer.

It is possible to utilize a spiral wound module (in the case of a supported membrane) which includes a non-porous separating layer membrane mounted on a porous support layer and a carrier layer, the  
10 assembly being typically folded and bonded or sealed along all the edges but an open edge - to form a bag-like unit which preferably has the separating layer on the outside. A cloth spacer, serving as the permeate or discharge channel is placed within the bag-like unit. The discharge channel projects from the open end of the unit.

There is then placed on one face of the bag-like unit, adjacent to the separating layer, and coterminous  
15 therewith, a feed channel sheet - typically formed of a plastic foraminous net.

The so-formed assembly is wrapped around a preferably cylindrical conduit which bears a plurality of perforations in the wall preferably in a linear array which is as long as the width of the bag-like unit. The projecting portion of the discharge channel of the bag-like unit is placed over the perforations of the conduit; and the bag-like unit is wrapped around the conduit to form a spiral wound configuration. It will be apparent  
20 that, although only one feed channel is present, the single feed channel in the wound assembly will be adjacent to two faces of the membrane layer. The spiral wound configuration may be formed by wrapping the assembly around the conduit a plurality of times to form a readily handlable unit. The unit is fitted within a shell (in manner comparable to a shell-and-tube heat exchanger) provided with an inlet at one end and an outlet at the other. A baffle-like seal between the inner surface of the shell and the outer surface of the  
25 spiral-wound unit prevents fluid from bypassing the operative membrane system and insures that fluid enters the membrane system principally at one end. The permeate passes from the feed channel, into contact with the separating layer and thence therethrough, into the permeate channel and thence therealong to and through the perforations in the conduit through which it is withdrawn as net permeate.

In the case of the spiral wound membrane, charge liquid is permitted to pass through the plastic net  
30 which serves as a feed channel and thence into contact with the non-porous separating membranes. The liquid which does not pass through the membranes is withdrawn as retentate. The liquid or vapor which permeates the membrane passes into the volume occupied by the permeate spacer and through this permeate channel to the perforations in the cylindrical conduit through which it is withdrawn from the system.

35 In another embodiment, it is possible to utilize the system of this invention as a tubular or hollow fibre. In this embodiment, the porous support (polyacrylonitrile) layer may be extruded or spun as a fine tube with a wall thickness of typically 0.001-0.1mm. The extruded tubes are passed through a bath of polyvinyl alcohol/polyacrylic acid which is cured in situ on the tubes. A bundle of these tubes is secured (with an epoxy adhesive) at each end in a header; and the fibres are cut so that they are flush with the ends of the  
40 header. This tube bundle is mounted within a shell in a typical shell-and-tube assembly.

In operation, the charge liquid may be admitted to the tube side and passes through the inside of the tubes and exits as retentate. During passage through the tubes, permeate passes through the non-porous separating layer and permeate is collected in the shell side.

45 In this embodiment, it will be apparent that the system may not normally include a carrier layer.

#### PERVAPORATION

60 It is a feature of the non-porous separating layer that it is found to be particularly effective when used in a pervaporation process. In pervaporation, a charge liquid containing a more permeable and a less permeable component is maintained in contact with a non-porous separating layer; and a pressure drop is maintained across that layer. The charge liquid dissolves into the membrane and diffuses therethrough. The permeate which passes through the membrane and exits as a vapor may be recovered by condensing at  
55 low temperature or alternatively may be swept away by use of a moving stream of gas. Preferably, the permeate side of the membrane is maintained at a low pressure, typically 2 mm. Hg.

For general background on pervaporation, note US 4,277,344; US 4,039,440; US 3,926,798; US 3,959,247; US 4,035,291; etc.

In practice of the pervaporation process of this invention, the charge solution at 40°C - 120°C, say 70°C may be passed into contact with the non-porous separating layer of the membrane of this invention. A pressure drop of about one atmosphere is commonly maintained across the membrane. Typically, the feed or charge side of the membrane is at about atmospheric pressure and the permeate or discharge side of the membrane is at a pressure of about 0.1-2.7KPa preferably 0.1-1.35KPa say 0.24KPa.

The permeate which passes through the membrane includes alcohol and a small proportion of the other components of the charge liquid. Typically, the permeate contains 90 - 99.9 w%, say 99 w% alcohol. Permeate is recovered in vapor phase.

Pervaporation may typically be carried out at a flux of about 0.04 - 2.2, say 0.13 kilograms per square meter per hour (kmh). Typically, the units may have Selectivity (measured in terms of w% alcohol in the permeate) of 96 - 99.9, say 99.3%. In terms of e.g. w% DMC in the permeate, the Selectivity may be 0.7 - 7.4, say 0.76 w%.

The Separation Factor S or Sep which represents the ability of the membrane to separate is calculated as follows:

$$S = \frac{\left( \frac{X_n}{X_m} \right)_p}{\left( \frac{X_n}{X_m} \right)_f}$$

wherein  $X_n$  and  $X_m$  are the weight fractions of alcohol and oxygenate components respectively in the permeate (p) and the feed (f). A system showing no separation at all would have a Separation Factor of 1; and a system showing perfect 100% separation would have a Separation Factor of infinity. The process of the instant invention may commonly have a Separation Factor of about 4 - 60, typically 20 - 60, say about 50.

It is a feature of this invention that the novel membrane may be particularly useful in pervaporation processes for concentrating a charge composition containing (i) an alcohol and (ii) oxygenate selected from the group consisting of organic ethers, aldehydes, ketones, and esters.

The oxygenate may be:

- (i) an organic ether such as dimethyl ether, diethyl ether, di-n-propyl ether, di-n-butyl ether, methyl t-butyl ether, ethyl t-butyl ether, methyl t-amyl ether, ethyl t-amyl ether, etc.;
- (ii) an aldehyde such as acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, etc.;
- (iii) a ketone such as acetone, methyl ethyl ketone, diethyl ketone, etc.; or
- (iv) an ester such as methyl acetate, methyl propionate, methyl butyrate, methyl benzoate, dimethyl carbonate, diethyl carbonate, etc.

The alcohol may typically be methanol or ethanol.

It will be clear to those skilled in the art that the process of this invention may find particular use when the charge mixture to be treated is a reaction product wherein one of the components to be separated is unreacted charge component. A typical such charge mixture is the charge solution attained from the reaction of methanol, oxygen, and carbon monoxide wherein the mixture may contain unreacted methanol and product dimethyl carbonate (DMC). Another illustrative charge mixture is that attained from the reaction of methanol and isobutene wherein the reaction mixture may contain methanol and methyl t-butyl ether (MTBE).

These charge mixtures may have been subjected to preliminary separation, e.g. distillation, to yield, for example, an azeotrope of methanol and dimethyl carbonate.

Other charge mixtures may include (i) methyl acetate-methanol, (ii) ethyl acetate-ethanol, etc.

Practice of the process of this invention will be apparent to those skilled in the art from inspection of the following examples wherein, as elsewhere in this specification, all parts are parts by weight unless otherwise stated.

EXAMPLE I

In this example, which represents the best mode presently known of carrying out the process of this invention, the porous support layer is the DUY-L brand of polyacrylonitrile membrane mounted on an inert carrier layer. The porous support layer has a molecular weight cut-off of 40,000. The separating layer is formed from an aqueous solution containing 10g of 7 w% polyvinyl alcohol PVA (M.W. of 115,000) and 10g of 7 w% polyacrylic acid PAA (M.W. of 250,000). This 50/50 mixture is stirred until homogeneous and spread onto the polyacrylonitrile microporous support to form a film 4 mils thick. The assembly is cured in an oven for 3 minutes at 150° C.

The membrane is evaluated in a pervapor ation cell to which the charge at 70 °C is a mixture containing 27.4 w% dimethyl carbonate (DMC) and 72.6 w% methanol.

The concentration of DMC in the Permeate is only 0.7 w%. The Separation Factor is 53.5 and the Flux is 0.13 kmh.

EXAMPLES II-III

In this series of examples the conditions of Example I are duplicated except that in Example II, the weight ratio of PVA/PAA is 70/30 and in Example III, it is 30/70.

EXAMPLES IV-VI

In this series of examples, the conditions of Example I are duplicated except that the curing temperature of the PVA/PAA membrane is varied.

EXAMPLES VII-IX

In this series of examples, the conditions of Example I are duplicated except that the separating layer is prepared from polymers of different molecular weight.

The following Table sets forth (i) the weight ratio of PVA/PAA, (ii) the molecular weight of the PVA/PAA (x 1000), (iii) the curing temperature °C, (iv) the concentration w% of DMC in the feed, (v) the concentration w% of DMC in the Permeate, (vi) the Separation Factor, and (vii) the Flux (kmh).

TABLE

| Example | Membrane         |                      |                |              | Performance      |      |      |
|---------|------------------|----------------------|----------------|--------------|------------------|------|------|
|         | PVA/PAA<br>Ratio | PVA/PAA<br>(MWx1000) | Curing<br>T °C | Feed<br>%DMC | Permeate<br>%DMC | Sep  | Flux |
| I       | 50/50            | 115/250              | 150            | 27.4         | 0.7              | 53.5 | 0.13 |
| II      | 70/30            | 115/250              | 150            | 29.3         | 1.9              | 21.4 | 0.12 |
| III     | 30/70            | 115/250              | 150            | 27.4         | 1.3              | 28.7 | 0.04 |
| IV      | 50/50            | 115/250              | 150            | 27.4         | 0.7              | 53.5 | 0.13 |
| V       | 50/50            | 115/250              | 140            | 27.3         | 1.8              | 20.5 | 0.03 |
| VI      | 50/50            | 115/250              | 125            | 27.3         | 1.5              | 24.7 | 0.03 |
| VII     | 50/50            | 115/250              | 110            | 27.3         | 2.4              | 15.3 | 0.04 |
| VIII    | 50/50            | 96/250               | 150            | 26.6         | 7.4              | 4.5  | 1.62 |
| IX      | 50/50            | 96/90                | 150            | 26.6         | 6.8              | 5.0  | 2.26 |
| X       | 50/50            | 115/90               | 150            | 26.6         | 1.5              | 23.8 | 0.12 |
| XI      | 50/50            | 115/250              | 150            | 27.4         | 0.7              | 53.5 | 0.13 |



From the above Table, the following conclusions may be drawn:

- (i) Best Separation Factor is attained in Example I using a 50/50 membrane (cured at 150.C) of PVA of  $\bar{M}_n$  of 115,000 and PAA of  $\bar{M}_n$  of 250,000;
- (ii) Best Flux is attained in Example VIII using a 50/50 membrane (cured at 150.C) of PVA of  $\bar{M}_n$  of 96,000 and PAA of  $\bar{M}_n$  of 90,000;
- (iii) As the curing temperature rises from 110 °C -150 °C, the Separation improves and highest flux is attained by use of membranes cured at higher temperature;
- (iv) At constant molecular weight of 96,000 of PVA, better Separation and Flux are attained using PAA of lower molecular weight; and
- (v) At constant molecular weight of of PVA, best Separation is attained using PAA of higher molecular weight.

## Claims

1. A method of separating or partially separating into its components, a charge composition containing (i) an alcohol having less than three carbon atoms and (ii) an oxygenate selected from organic ethers, aldehydes, ketones, and esters characterized by passing said charge composition into contact with a first side of a non-porous membrane separating layer comprising a blend of a polyvinyl alcohol and a polyacrylic acid on a polyacrylonitrile support layer; maintaining a pressure drop across said non-porous separating layer from said first (high pressure) side to a second (low pressure) side, whereby at least a portion of alcohol in said charge composition and a lesser portion of oxygenate pass by pervaporation through said non-porous separating layer as a lean mixture containing more alcohol and less oxygenate than are present in said charge composition and leaving a rich liquid containing less alcohol and more oxygenate than are present in said charge composition; and recovering said lean mixture in vapor phase at a pressure below the vapor pressure thereof, as permeate from the low pressure side of said non-porous separating layer.
2. A method according to Claim 1 characterized in that the polyacrylonitrile support layer has a molecular weight cut-off of 20,000 to 40,000.
3. A method according to Claim 1 or 2 characterized in that the polyvinyl alcohol of the separating layer has a molecular weight  $\bar{M}_n$  of 96,000 to 115,000.
4. A method according to any of Claims 1 to 3 characterized in that the polyacrylic acid of the separating layer has a molecular weight  $\bar{M}_n$  of 90,000 to 250,000.
5. A method according to any one of Claims 1 to 4 characterized in that the temperature of the charge composition is 40 to 120°C, the pressure on the high pressure side is ambient pressure, and the pressure on the low pressure side is 0.1 to 2.7 KPa.
6. A method according to any of Claims 1 to 5 characterized in that the alcohol is methanol and the oxygenate is dimethyl carbonate.
7. A method according to any one of Claims 1 to 5 characterized in that the alcohol is methanol and the oxygenate is methyl t-butyl ether.



(19)



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**London W1M 8AH(GB)**(54) **Membrane process for separation of organic liquids.**

(57) A charge composition containing (i) an alcohol having less than three carbon atoms and (ii) an oxygenate selected from organic ethers, aldehydes, ketones, and esters is passed into contact with a first side of a non-porous membrane separating layer comprising a blend of a polyvinyl alcohol and a polyacrylic acid on a polyacrylonitrile support layer; with a pressure drop across the non-porous separating layer from the first (high pressure) side to a second (low pressure) side. At least a portion of alcohol from the charge composition and a lesser portion of oxygenate pass by pervaporation through the non-porous separating layer as a lean mixture containing more alcohol and less oxygenate than are present in said charge composition, leaving a rich liquid containing less alcohol and more oxygenate than are present in said charge composition; the lean mixture, in vapor phase at a pressure its vapor

pressure being recovered as permeate from the low pressure side of the non-porous separating layer.

**EP 0 423 949 A3**



European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 90 31 0398

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |                              |  |
|---|---|------------------------------|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim            | CLASSIFICATION OF THE APPLICATION (Int. Cl.5)  |
| Y   | MAKROMOL. CHEM., vol. 188, 1987, pages 1973-1984;<br>T.Q. NGUYEN et al.: "Synthesis of membranes for the dehydration of water-acetic acid mixtures by pervaporation, 1: Polymer material selection"<br>* Summary; page 1976, lines 15-31; tables 2,3; page 1978, line 1 - page 1980, line 7 * | 1-7                          | B 01 D 61/36<br>C 07 C 29/76<br>B 01 D 71/38<br>B 01 D 71/40<br>B 01 D 69/12<br>C 07 C 68/08<br>C 07 C 41/34<br>C 07 C 45/78<br>C 07 C 67/48 |
| Y   | EP-A-0 331 846 (TEXACO DEV. CORP.)<br>* Abstract; claims 1,5,6,9; page 6, lines 47-48; page 9, lines 25-38 *  | 1-7                          |  |
| P,A   | EP-A-0 381 476 (TEXACO DEV. CORP.)(08-08-1990)<br>* Abstract; claims 1,6; page 5, line 18 - page 6, line 14; example 1 *  | 1-5                          |  |
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| Place of search   |   | Date of completion of search | Examiner   |
| The Hague   |   | 24 May 91                    | HOORNAERT P.G.R.J.   |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X: particularly relevant if taken alone<br>Y: particularly relevant if combined with another document of the same category<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying the invention<br>E: earlier patent document, but published on, or after the filing date<br>D: document cited in the application<br>L: document cited for other reasons<br>&: member of the same patent family, corresponding document |   |                              |  |



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Application Number

EP 90 31 0398

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